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Research article

Evaluation of an alternative method for wastewater treatment containing pesticides using solar photocatalytic oxidation and constructed wetlands

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ABSTRACT

The present study proposes an integrated system based on the synergetic action of solar photocatalytic oxidation with surface flow constructed wetlands for the purification of wastewater contaminated with pesticides. Experiments were conducted at pilot scale using simulated wastewater containing the herbicide clopyralid. Three photocatalytic methods under solar light were investigated: the photo-Fenton and the ferrioxalate reagent as well as the combination of photo-Fenton with TiO_2 P25, which all led to similar mineralization rates. The subsequent treatment in constructed wetlands resulted in further decrease of DOC and inorganic ions concentrations, especially of NO_3^-. Clopyralid was absent in the outlet of the wetlands, while the concentration of the detected intermediates was remarkably low. These findings are in good agreement with the results of phytotoxicity of the wastewater, after treatment with the ferrioxalate/wetlands process, which was significantly reduced. Thus, this integrated system based on solar photocatalysis and constructed wetlands has the potential to effectively detoxify wastewater containing pesticides, producing a purified effluent which could be exploited for reuse applications.

1. Introduction

The uncontrolled use of pesticides during the 20th century due to widespread intensive agriculture, is polluting water resources. Although their necessity in agriculture is undeniable, pesticides can cause significant problems upon their release to the environment (Zhang and Pagilla, 2010). United Nations estimate that less than 1% of all pesticides used in agriculture actually reaches the crops. The remaining contaminates the land, the air and particularly the water. These xenobiotics are in many cases toxic and non-biodegradable, with the potential to cause adverse acute or chronic toxic health effects to non-target organisms and to accumulate in the environment through the global trophic network with unpredictable consequences (NATO, 2012). Increasing concern involves the importance of small residues of pesticides, often suspected of causing acute neurologic toxicity, chronic neurodevelopmental impairment, cancer and endocrine dysfunction (Arias-Estevez et al., 2008; Readman et al., 1993; Sharma et al., 2008; Thurman and Meyer, 1996).

Thus, the need for applying alternative methods for wastewater purification, is progressively becoming a priority for government agencies, regulatory agencies and the general public. However, the wide range of pesticides in use makes research extremely difficult for producing a single method for the removal of pesticides that applies universally (Kock-Schulmeyer et al., 2013). In view of this, it is necessary to develop sustainable technologies that promote the degradation of such bio-recalcitrant organic compounds.

Advanced oxidation processes (AOPs) are characterized by the production of hydroxyl radicals (OH•), one of the most powerful oxidants, which can easily attack organic molecules leading to the production of organic peroxide-radicals and their final conversion to CO_2, H_2O and inorganic species (Malato et al., 2009). AOPs often take place under mild operating conditions and are considered to be promising technologies, allowing the contribution of renewable sources of energy (solar energy) to the process of environmental cleaning and restoration. Among these, heterogenous and

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homogenous solar photocatalytic detoxification methods (TiO_2/H_2O_2/UV-A, Fe^{3+}/H_2O_2/UV-A, Vis) have gained great interest for the treatment of wastewater containing pesticides (Fagan et al., 2016).

Constructed wetlands on the other hand, are engineered systems that have been designed and constructed to utilize natural processes involving wetland vegetation, soils and their associated microbial assemblages to assist in treating wastewater. They are designed to take advantage of many of the processes that occur in natural wetlands, but do so within a more controlled environment (Vymazal and Bfezinova, 2015). They have the ability to efficiently treat a variety of wastewaters, removing organics, suspended solids, pathogens, nutrients and heavy metals, while their construction and maintenance cost is relatively low, since they are practically self-sufficient (Antoniadis et al., 2007; Papadimitriou et al., 2010).

In this work, a low cost treatment system based on the combination and the synergetic action of solar photocatalytic oxidation with surface flow constructed wetlands is developed (Fig. 1), to investigate its ability to be used as an alternative process of treating toxic, non-biodegradable pollutants, such as pesticides (Antoniadis et al., 2007; Arana et al., 2008). The positive interactions between solar photocatalysis and constructed wetlands in a combined system result, among others, to a reduction of establishment and operational costs, enhancement of biodegradability in wetlands, low concentrations of nitrate and phosphate ions, etc (Antoniadis et al., 2007). The current paper demonstrates the results from the experimental evaluation of this innovative system in the detoxification of simulated wastewater containing the herbicide clopyralid. Our group has already published data concerning photocatalytic mineralization of clopyralid in laboratory scale (Berberidou et al.). Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid) is a systemic herbicide from the chemical class of pyridine compounds, often detected in drinking water (Donald et al., 2007). It is used to control annual and perennial broadleaf weeds in certain crops and turf and provides control of some brush species on rangeland and pastures. It may be persistent in soil under anaerobic conditions and with low microorganism content, with half-life ranging from 15 to more than 280 days (Corredor et al., 2006). It presents high solubility in water and is particularly stable against hydrolysis and photolysis. Its chemical stability, along with its mobility, enables this herbicide to penetrate through soil, causing a long term contamination of ground and surface water supplies (Huang et al., 2004; Sakaliene et al., 2009). Clopyralid is hazardous to a number of endangered plant species, beneficial insects (Hassan et al., 1994) and toxic to certain mammals (Hayes et al., 1984).

Many studies indicate that a wide range of pesticides are readily degradable by means of heterogenous or homogenous photocatalysis. Often, the reduction or elimination of ecotoxicity under the investigated conditions is also reported, employing microorganisms, i.e. *Vibrio fischeri, Daphnia magna etc.* Nonetheless, the potential residual toxicity of the treated wastewater on higher plants has rarely been investigated (Arana et al., 2008). This is a very important point since, the generated effluent, if effectively purified, could be exploited in reuse applications, i.e. irrigation. It has been clearly demonstrated in several studies that even if the parent compound is completely eliminated, the generated intermediates can be more toxic. In this study, after purification employing the integrated system photocatalytic oxidation/constructed wetlands, the use of higher plants (*Sorghum saccharatum*, *Lepidium sativum* and *Sorghum alba)* is reported for the evaluation of residual toxicity of wastewater containing clopyralid using a simple, sensitive and inexpensive test (Phytotoxkit, MicroBioTests Inc). According to our knowledge, this is the first report in which data concerning the reduction of phytotoxicity of clopyralid subjected to photocatalytic treatment, employing eukaryotic plants, are presented.

2. Materials and methods

2.1. Materials

Lontrel 100AS®, a commercial herbicide, (active ingredient: clopyralid, 10% w/v) was a product of Dow Agrosciences. Clopyralid (3,6-dichloro-pyridine-2-carboxylic acid, CAS No. 1702-17-6, M_r: 192 g mol^{-1}, Product No: 36758, Pestanal, analytical standard) was a product of Fluka (Sigma-Aldrich Laborchemicalien GmbH).

TiO_2 P25 was a product of Evonik Industries (anatase/rutile = 3.6/1, BET: 50 m^2 g^{-1}, nonporous). All other reagent-grade chemicals were purchased from Merck and were used without further purification.

2.2. Pilot scale photocatalytic experiments

Experiments were conducted at pilot scale using simulated

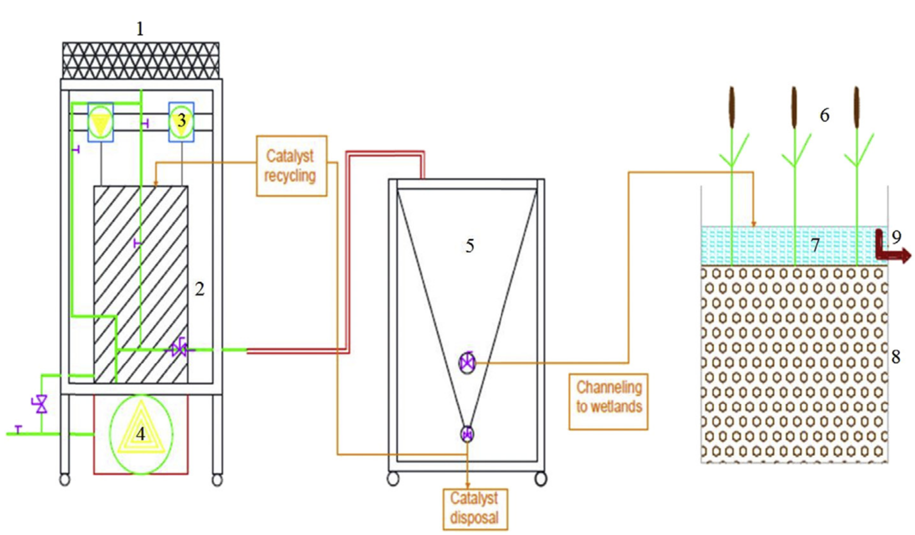

Fig. 1. Integration of solar photocatalysis with constructed wetlands for the purification of simulated wastewater containing pesticides: 1. photoreactor, 2. storage tank, 3. dosimetric pump, 4. pump, 5. Imhoff tank, 6. *Typha* spp. plants, 7. wastewater, 8. soil, 9. wetland outlet.

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